

## Influence on the growth temperature for one-dimensional GaN nanostructures by halide vapor-phase epitaxy

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High-quality one-dimensional GaN nanorods and nanowires were synthesized on Ni-coated c-plane sapphire substrates using halide vapor-phase epitaxy (HVPE). Their structure and optical properties were investigated by X-ray diffractometry, scanning and transmission electron microscopy, and photoluminescence techniques. A high density of straight and aligned one-dimensional GaN nanowires with a diameter of 80 nm was uniformly formed on the entire substrate at 700 °C. The X-ray diffraction patterns, transmission electron microscope images, and selected area electron diffraction patterns indicate that the one-dimensional GaN nanostructures are pure single crystals and preferentially oriented in the [001] direction. We observed high optical quality of GaN nanowires by photoluminescence analysis.

**Key words:** GaN, one-dimensional nanostructure, halide vapor-phase epitaxy, single crystal growth

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### Introduction

The discovery of carbon nanotubes [1] has drawn great attention to the fabrication of one-dimensional (1-D) nanostructures, such as, wires and rods [2, 3]. An understanding of such one-dimensional nanostructures is essential in testing the role of dimensionality and size in optical, electrical, mechanical, and magnetic properties. In addition, nanostructures have significant potential applications as interconnects in nanoelectronic devices [4]. Meanwhile, the miniaturization of devices represents a trend for both industrial manufacture and academic research. In this regard, 1-D nanostructures are interesting as building blocks toward the fabrication of various devices on a nano scale [5, 6]. Furthermore, theoretical calculations indicate that the chemical and physical properties of a nanostructure could be substantially superior to those of the bulk or a thin film [7]. The combination of these distinctive physical and chemical properties of GaN and unique advantages of nanostructures make GaN an excellent candidate for designing and fabricating nanodevices. Ga-based nitride semiconductors with a large band gap and strong chemical bonding have been extensively studied because of their versatile optoelectronic and electronic properties for devices [8]. There are reports on the formation of 1-D GaN structures using various methods by several groups [9-11]. Among these methods, especially, halide vapor-phase epitaxy (HVPE) has been widely used as a

growth method for both high quality GaN thin films produced at a high growth rate and reduction of the native defect concentration to non-degenerate levels which thus enables p-type doping, because HVPE growth occurs close to the thermodynamical equilibrium [12, 13]. Despite these advantages, there have been few reported <100 nm 1-D GaN nanowires using the HVPE. For growth control using this system, we need to understand the growth conditions with a vapor-liquid-solid (VLS) mechanism for the formation of 1-D GaN and the fabrication of defect-free GaN single crystals. In this study, we report on the formation of 1-D GaN nanostructures using Ni-coated single crystal sapphire substrates. By using an HVPE system, we effectively controlled the diameter size and type of 1-D GaN nanostructure through the growth conditions.

### Experimental Procedures

The growth of GaN nanowires was carried out in a horizontal hot-wall HVPE system. The 1-D GaN nanowires were grown by an HVPE method, which transports gallium created by decomposing gallium chloride under a flow of ammonia gas at high temperature. The Ni catalyst on the sapphire substrates was sputter coated. The Ga sources were placed 13 mm from the center of the hot zone, and a reaction of HCl gas and the N<sub>2</sub> carrier gas gave the Ga supply. This precursor was transported to the substrate area, where it was mixed with NH<sub>3</sub> diluted with N<sub>2</sub> gas to form GaN single crystal. In this process, the HCl flow rate was in the range of 1~5 sccm, and the NH<sub>3</sub> flow rate were 20~50 sccm and various temperatures were used. The total gas flow rate was kept at 500 sccm for all

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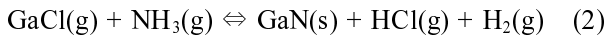
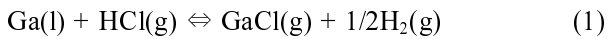
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experiments. After the furnace was cooled to room temperature, a light yellow layer was found on the surface of the substrate.

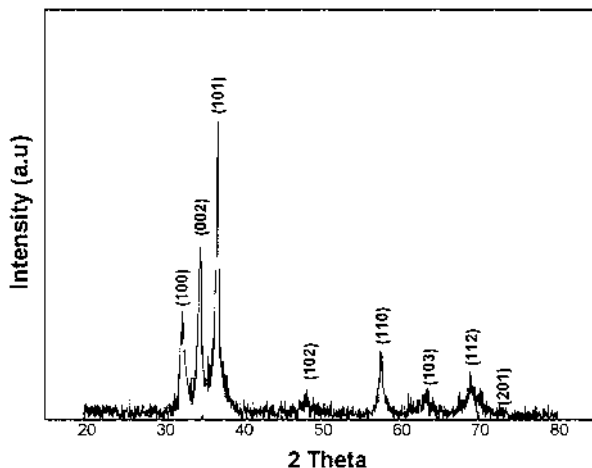
The morphologies and crystalline structure of the 1-D GaN on the substrate were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED). Photoluminescence (PL) spectra were also measured at room temperature using a He-Cd laser with 325 nm excitation to study the optical properties of the nanowires.

## Results and Discussion

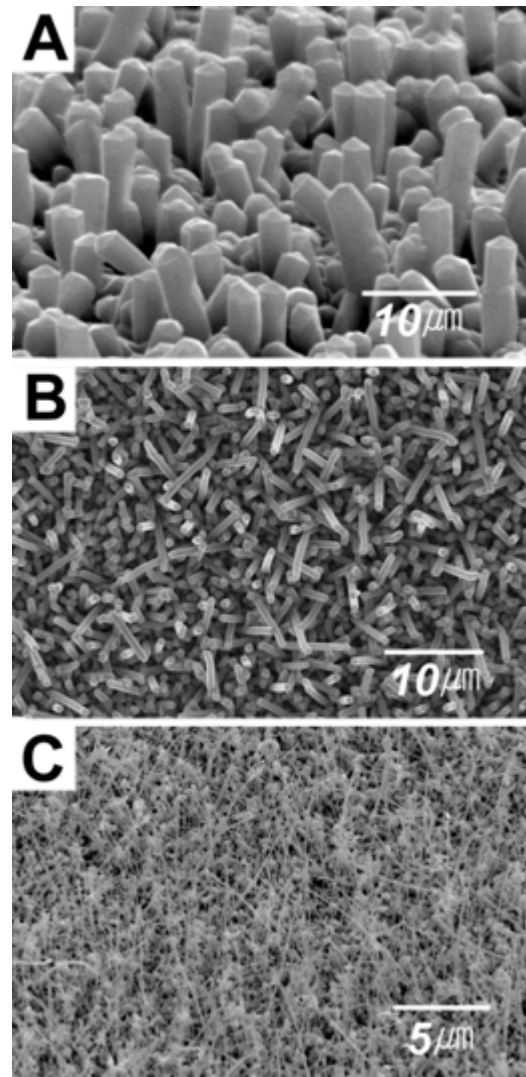
The use of HVPE is considered to be critical in making 1-D GaN nanostructures. The transported Ga atoms react with Cl gas through a reaction with HCl gas and then with  $\text{NH}_3$  to produce GaN crystalline phase with the following schematic reaction [14];



In this reaction, the  $\text{GaCl}_3$  serves as a thermodynamically-favorable transport medium for the formation of the GaN phase as well as acting as a doping reactant. Importantly, this process can produce defect-free single crystalline GaN nanowires, where the problem of defects has been a common problem in GaN thin film studies. Figure 1 shows an XRD pattern from GaN nanowires grown on a c-plane sapphire substrate by HVPE. The sharp diffraction peaks in the pattern indicate an hexagonal wurtzite structure with lattice constants of  $a = 0.3189$  nm and  $c = 0.5183$  nm, which agree with the reported values of bulk GaN [15]. In the XRD result, it is noted that the intensity from the (002) plane was higher than that from bulk crystals, and this is because of the preferred orientation c-plane growth



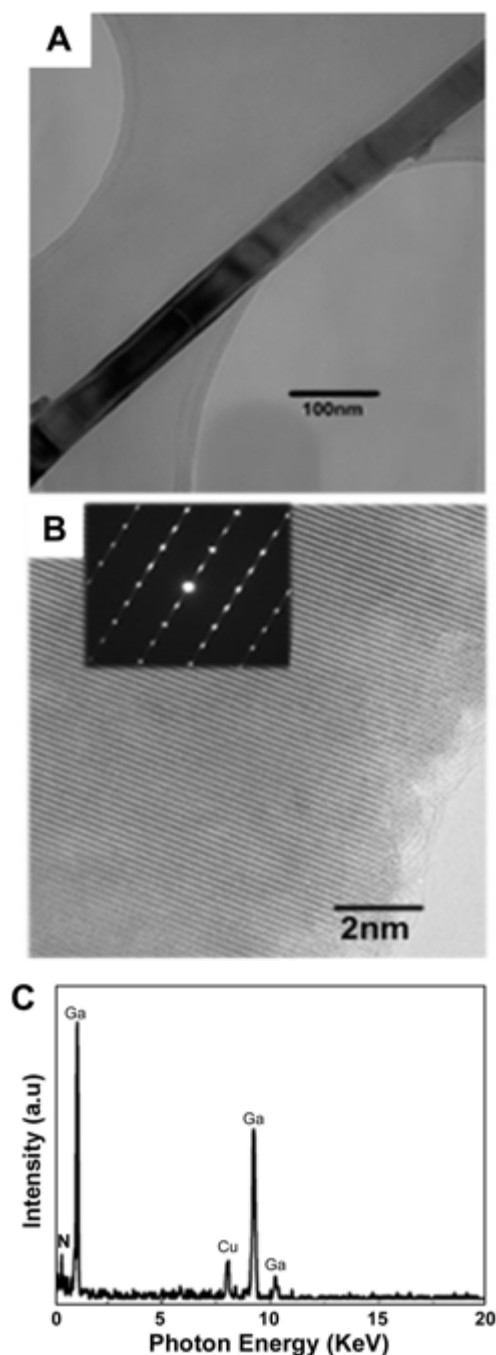
**Fig. 1.** XRD pattern of GaN nanowires on a sapphire substrate formed by HVPE.



**Fig. 2.** Typical SEM images of 1-D GaN rods and nanowires, grown on c-plane sapphire substrates at (A) 900°C, (B) 800°C, and (C) 700°C, respectively.

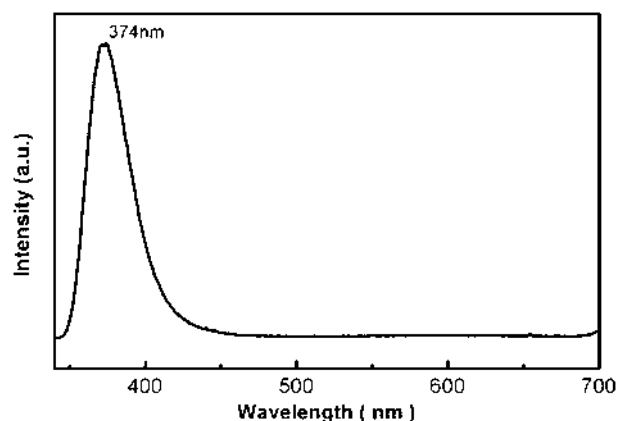
direction in hexagonal GaN structures. Generally, nanowires using a metallic catalyst (Ni is used in our experiments) by the VLS mechanism formed metal tips on the top of the nanowires. However, our nanowires do not retain their metal tips due to etching of the tips by the HCl gas produced from Eq. 2. Therefore metallic impurities do not appear in our XRD analysis. Figure 2 show typical SEM images of 1-D GaN nanostructures grown at 900°C (Fig. 2A), 800°C (Fig. 2B), and 700°C (Fig. 2C) with crystal diameter sizes of 3 μm, 650 nm, and 80 nm, respectively.

A high density of straight and aligned 1-D GaN rods and nanowires were uniformly formed on the entire substrate. Many research groups have reported that the growth temperature of GaN nanowires and thin films is above 900°C [6-10]. However, in this study, the GaN nanowires were grown at 700°C due to the higher deposition rate [16]. Also, the type of GaN rod and wire varied with the growth temperature. This result



**Fig. 3.** (A) TEM image of GaN nanowires, (B) High resolution TEM image of single crystalline GaN nanowire and inset is the corresponding electron diffraction patterns taken along the  $\langle 100 \rangle$  zone axis, (C) EDS spectrum of the nanowire.

suggests that the primary growth direction differed depending on the growth temperature. At a higher temperature, the  $[110]$  growth direction was preferred rather than the  $[001]$  direction in our system. Figure 3 A shows a low magnification TEM image of GaN nanowires where a linear segment was crystalline with a diameter of 80 nm. The HR-TEM image (Figure 2B) was taken parallel to the long axis of the wire, the  $[001]$  direction. The inset is an SEAD pattern taken along the  $[100]$  zone axis, which shows that the nano-



**Fig. 4.** PL spectrum of a GaN nanowire.

wires have a wurtzite structure with a  $[001]$  growth direction, in good agreement with the XRD results. Figure 3C shows from the energy dispersive spectroscopy (EDS) analysis that the nanoparticle on the tip consisted mainly of Ni, Ga, and N, but that the nanowire was only composed of Ga and N. The molecular ratio of Ga/N in the nanowire calculated from the EDS data was close to that of a bulk GaN crystal. Thus, these data from SEM, EDS, and TEM analyses are consistent. In general for VLS growth, the diameter size of nanowires is dependent on the particle size of the metallic catalyst [4]. However, by contrast in our study, the diameter of 1-D GaN was found to vary with the growth temperature. We consider that the growth of our nanowires was closed rather than a result of the direct vapor-phase growth, which is the proposed VLS mechanism. However, growth of our nanowires required the catalyst. This phenomenon has not been addressed yet.

Finally, we carried out studies of the optical properties of the GaN nanowires. Figure 4 shows the PL spectrum of GaN nanowires measured at room temperature. With a He-Cd laser excitation at 325 nm, a band-edge emission at 374 nm (3.31 eV) is observed. Significantly, the well-known defect-induced yellow emission band is not observed here, indicating the high optical quality of GaN nanowires obtained in the present study.

## Conclusions

In this study, high-quality 1-D GaN rods and nanowires were synthesized on Ni-coated c-plane sapphire substrates using an HVPE system. A high density of straight and aligned 1-D GaN nanowires was grown at 700 °C. We have optimized the synthetic growth conditions, to reduce the dependence of the diameter of 1-D GaN nanowires on the growth temperature. The resulting nanowires have a preferred  $[001]$  growth direction. The strong photoluminescence of the nanowires in the blue region suggests possible applications

in optoelectronic nanodevices. Therefore well-controlled 1-D GaN nanostructures offer good opportunities for making direct nanodevices, such as nanowire-based field effect transistor, light emitting diodes, and sensors.

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